

# catena-Poly[[tetraaqua- $\mu$ -aqua-bis( $\mu_4$ -pyrimidine-2-carboxylato)tetralithium]dichloride]

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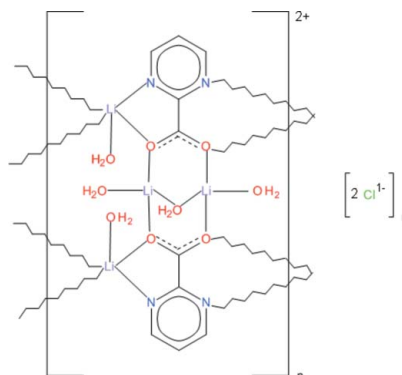
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.044;  $wR$  factor = 0.147; data-to-parameter ratio = 18.5.

The asymmetric unit of the title compound,  $[\text{Li}_4(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_5]\text{Cl}_2$ , contains two  $\text{Li}^{\text{I}}$  cations, one with a distorted trigonal-bipyramidal and the other with a distorted tetrahedral coordination geometry. Two symmetry-related asymmetric units constitute a building block of the structure, in which both ligand carboxylate O atoms are bidentate and bridge the metal ions, forming a divalent cation. Charge balance is maintained by two chloride anions. The building blocks, bridged by  $\text{Li}^{\text{I}}$  cations, form cationic ribbons with chloride anions in the space between them. The ribbons propagate in  $[010]$  and are held together by a network of weak  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds which operate in the space between adjacent ribbons.

## Related literature

For the structure of a Li complex with pyrimidine-2-carboxylate and nitrate ligands, see: Starosta & Leciejewicz (2011). The structure of a  $\text{Li}^{\text{I}}$  complex with pyrimidine-4-carboxylate and water ligands was reported recently by Starosta & Leciejewicz (2012).



## Experimental

### Crystal data

$[\text{Li}_4(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_5]\text{Cl}_2$   
 $M_r = 434.93$   
 Monoclinic,  $C2/c$   
 $a = 22.084$  (4) Å  
 $b = 8.0773$  (16) Å  
 $c = 10.814$  (2) Å  
 $\beta = 94.08$  (3)°

$V = 1924.1$  (7) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.39$  mm<sup>-1</sup>  
 $T = 293$  K  
 $0.37 \times 0.24 \times 0.18$  mm

### Data collection

Kuma KM4 four-circle diffractometer  
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2008)  
 $T_{\text{min}} = 0.917$ ,  $T_{\text{max}} = 0.935$   
 2964 measured reflections

2819 independent reflections  
 1781 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$   
 3 standard reflections every 200 reflections  
 intensity decay: 2.3%

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.147$   
 $S = 1.02$   
 2819 reflections  
 152 parameters  
 4 restraints

H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.51$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.36$  e Å<sup>-3</sup>

Table 1

Selected bond lengths (Å).

Li1—O1	2.069 (3)	Li2—O21	2.140 (6)
Li1—N1	2.175 (4)	Li2—O22	1.915 (4)
Li1—O3	1.987 (4)	Li2—O2 <sup>ii</sup>	1.968 (4)
Li1—O2 <sup>i</sup>	2.029 (4)	Li2—O1	1.993 (4)
Li1—N3 <sup>i</sup>	2.221 (4)		

Symmetry codes: (i)  $x, -y + 2, z + \frac{1}{2}$ ; (ii)  $-x, y, -z + \frac{1}{2}$ .

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O22—H222 <sup>iii</sup> ···O3	0.89 (2)	2.16 (3)	2.841 (3)	133 (3)
O22—H221 <sup>iii</sup> ···Cl1 <sup>iii</sup>	0.87 (2)	2.36 (2)	3.212 (2)	167 (3)
O3—H31 <sup>i</sup> ···Cl1	0.83 (4)	2.35 (4)	3.1381 (19)	158 (3)
O3—H32 <sup>i</sup> ···Cl1 <sup>iv</sup>	0.86 (4)	2.29 (4)	3.1429 (19)	168 (4)
O21—H211 <sup>i</sup> ···Cl1 <sup>v</sup>	0.84 (3)	2.45 (3)	3.288 (2)	175 (3)

Symmetry codes: (iii)  $-x, y, -z + \frac{3}{2}$ ; (iv)  $x, -y + 1, z - \frac{1}{2}$ ; (v)  $-x, -y + 1, -z + 1$ .

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: QM2084).

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## References

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Starosta, W. & Leciejewicz, J. (2012). *Acta Cryst.* **E68**, m1065–m1066.

## supplementary materials

*Acta Cryst.* (2012). E68, m1369–m1370 [doi:10.1107/S1600536812041955]

## **catena-Poly[[tetraaqua- $\mu$ -aqua-bis( $\mu_4$ -pyrimidine-2-carboxylato)tetralithium]dichloride]**

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### **Comment**

The asymmetric cell of the title compound contains two symmetry independent  $\text{Li}^{\text{I}}$  ions, one deprotonated pyrimidine-2-carboxylato ligand molecule, three symmetry independent water molecules which are coordinated to metal ions and one chloride anion. The latter maintains charge balance in the cell. Two symmetry related cells form a molecular moiety which can be visualized as a building unit of the structure (Fig. 1). The ligand bridges Li ions in a  $\mu_4$  mode using both its carboxylate O atoms which act as bidentate. Ligand bonding groups N1,O1 and N3,O2 chelate  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  ions; the O1 and O2 atoms are also bonded to  $\text{Li}^{\text{II}}$  and  $\text{Li}^{\text{I}}$  ions, respectively. Since the  $\text{Li}^{\text{I}}$  and  $\text{Li}^{\text{II}}$  ions are also coordinated by bonding groups from adjacent symmetry related ligands, a  $-\text{Li}^{\text{II}}-\text{O2}-\text{O1}-\text{Li}^{\text{I}}-\text{O2}^{\text{III}}-\text{Li}^{\text{I}}-$  bridging pathway is formed. Apart from two N,O bonding groups,  $\text{Li}^{\text{I}}$  coordination is completed by an aqua O3 atom. On the other hand, pairs of adjacent symmetry related  $\text{Li}^{\text{II}}$  and  $\text{Li}^{\text{II}}$  ions are bridged by an aqua O21 atom while the other coordinated to them aqua O22 and O22<sup>i</sup> atoms are not bridging. Symmetry code: <sup>i</sup>  $-x, y, -z + 1/2$ ; <sup>ii</sup>  $x, -y + 2, z - 1/2$ ; <sup>iii</sup>  $x, -y + 2, z + 1/2$ . Adjacent moieties linked along the  $\text{Li}^{\text{I}}$  bridging pathway form a cationic ribbon propagating in the unit cell *b* direction (Fig. 2). Chloride anions are located in the space between adjacent ribbons. Fig. 1 shows, that a ribbon can be visualized as built of centro-symmetric molecular clusters in which Li ions form a tetrameric entities additionally connected by  $\text{Li}^{\text{II}}-\text{O21}-\text{Li}^{\text{II}}$  bridges. The  $\text{Li}^{\text{I}}$  ion exhibits a distorted trigonal bipyramidal coordination environment in which O1, O3 and N3<sup>iii</sup> atoms form an equatorial plane with a  $\text{Li}^{\text{I}}$  ion 0.0619 (2) Å out of it; N1 and O2<sup>iii</sup> atoms are at apical positions. The coordination of the  $\text{Li}^{\text{II}}$  ion is strongly distorted tetrahedral. The Li—O and Li—N bond distances (Table 1) are close to those reported in the structures of a Li complex with the title and nitrate ligands (Starosta & Leciejewicz, 2011) and pyrimidine-4-carboxylate and water ligands (Starosta & Leciejewicz, 2012). The pyrimidine ring is planar with r.m.s. of 0.0071 (1) Å; the C7/O1/O2 makes with it a dihedral angle of 5.8 (1)°. Weak hydrogen bonds in which water O atoms are as donors and chloride anions act as acceptors operate between adjacent ribbons (Table 2).

### **Experimental**

1 mmol of methyl pyrimidine-2-carboxylate and ca 2 mmol of lithium hydroxide dissolved in 50 ml of hot, doubly distilled water were boiled under reflux with stirring for twenty hours. After evaporation to dryness at room temperature the polycrystalline material was dissolved in 50 ml of water. The solution was titrated with 1 N HCl until the pH reached 6.0 and then stirred for 3 h at ca 320 K. Left to crystallize at room temperature, colourless single-crystal blocks deposited after a week. They were washed with cold methanol and dried in the air.

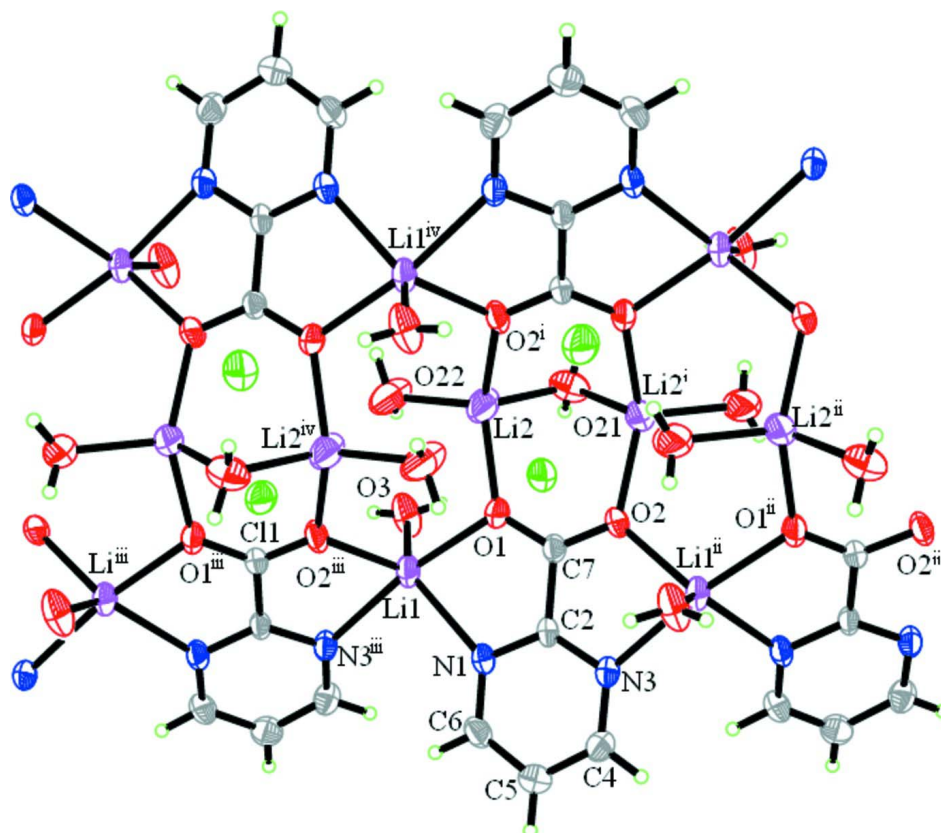
### **Refinement**

Hydrogen atoms belonging to water molecules were located in a difference map and refined isotropically, while three H atoms attached to pyrimidine C atoms were located at calculated positions and treated as riding on the parent atoms with

C—H=0.93 Å and  $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C})$ .

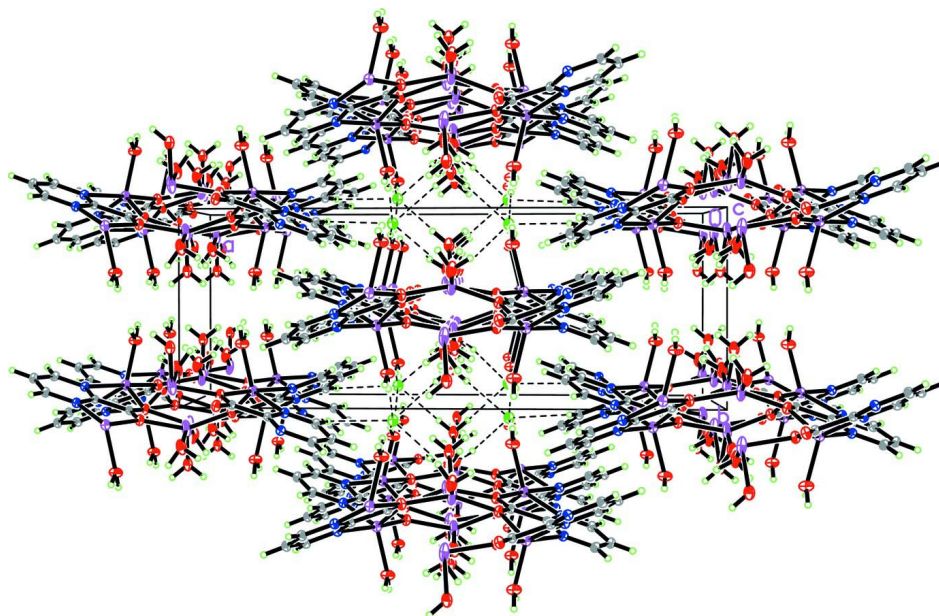
### Computing details

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software* (Kuma, 1996); data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).



**Figure 1**

A fragment of a cationic ribbon of the title compound with atom labelling scheme and 50% probability displacement ellipsoids. Symmetry code: <sup>i</sup>  $-x, y, -z + 1/2$ ; <sup>ii</sup>  $x, -y + 2, z - 1/2$ ; <sup>iii</sup>  $x, -y + 2, z + 1/2$ ; <sup>iv</sup>  $-x, -y + 2, z + 1$ .

**Figure 2**

The alignment of cationic ribbons and chloride anions in the structure of the title compound viewed along the unit cell *b* direction.

**catena-Poly[[tetraaqua- $\mu$ -aqua-bis( $\mu_4$ -pyrimidine-2-carboxylato)tetalithium] dichloride]**

*Crystal data*

$[\text{Li}_4(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_2(\text{H}_2\text{O})_5]\text{Cl}_2$

$M_r = 434.93$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 22.084\ (4)\ \text{\AA}$

$b = 8.0773\ (16)\ \text{\AA}$

$c = 10.814\ (2)\ \text{\AA}$

$\beta = 94.08\ (3)^\circ$

$V = 1924.1\ (7)\ \text{\AA}^3$

$Z = 4$

$F(000) = 888$

$D_x = 1.501\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation,  $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 25 reflections

$\theta = 6\text{--}15^\circ$

$\mu = 0.39\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Block, colourless

$0.37 \times 0.24 \times 0.18\ \text{mm}$

*Data collection*

Kuma KM4 four-circle  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

profile data from  $\omega/2\theta$  scans

Absorption correction: analytical

(*CrysAlis RED*; Oxford Diffraction, 2008)

$T_{\min} = 0.917$ ,  $T_{\max} = 0.935$

2964 measured reflections

2819 independent reflections

1781 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\max} = 30.1^\circ$ ,  $\theta_{\min} = 1.9^\circ$

$h = -31 \rightarrow 31$

$k = -11 \rightarrow 0$

$l = 0 \rightarrow 15$

3 standard reflections every 200 reflections

intensity decay: 2.3%

# Refinement

Refinement on  $F^2$ 

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.044$ 
 $wR(F^2) = 0.147$ 
 $S = 1.02$ 

2819 reflections

152 parameters

4 restraints

Primary atom site location: structure-invariant  
direct methods

Secondary atom site location: difference Fourier  
map

Hydrogen site location: inferred from  
neighbouring sites

H atoms treated by a mixture of independent  
and constrained refinement

 $w = 1/[\sigma^2(F_o^2) + (0.0879P)^2 + 1.2478P]$ 

where  $P = (F_o^2 + 2F_c^2)/3$ 
 $(\Delta/\sigma)_{\max} = 0.004$ 
 $\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$ 
 $\Delta\rho_{\min} = -0.36 \text{ e } \text{\AA}^{-3}$ 

# Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

# Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.08301 (6)	0.92604 (19)	0.37614 (11)	0.0321 (3)
O2	0.08768 (6)	0.96441 (19)	0.17202 (11)	0.0319 (3)
N3	0.20103 (7)	1.0854 (2)	0.20733 (13)	0.0277 (3)
N1	0.19897 (7)	1.0170 (2)	0.42115 (13)	0.0277 (3)
C6	0.25599 (9)	1.0720 (3)	0.43984 (17)	0.0326 (4)
H6	0.2752	1.0657	0.5191	0.039*
C2	0.17410 (7)	1.0274 (2)	0.30494 (14)	0.0232 (3)
C4	0.25768 (9)	1.1411 (3)	0.22901 (18)	0.0332 (4)
H4	0.2778	1.1836	0.1634	0.040*
C5	0.28729 (9)	1.1378 (3)	0.3457 (2)	0.0353 (4)
H5	0.3266	1.1781	0.3601	0.042*
Li1	0.13426 (15)	0.9162 (5)	0.5437 (3)	0.0323 (7)
O3	0.11355 (9)	0.6795 (2)	0.56747 (16)	0.0469 (4)
C7	0.10916 (8)	0.9673 (2)	0.28238 (14)	0.0239 (3)
O21	0.0000	0.6868 (4)	0.2500	0.0527 (6)
Li2	−0.00573 (17)	0.8841 (8)	0.3807 (4)	0.0590 (13)
Cl1	0.10829 (3)	0.57231 (8)	0.84542 (5)	0.04391 (17)
H211	−0.0286 (13)	0.622 (4)	0.230 (3)	0.064 (10)*
H32	0.1130 (18)	0.599 (5)	0.515 (4)	0.086 (12)*
H31	0.1170 (14)	0.627 (4)	0.634 (3)	0.065 (9)*
O22	−0.00669 (8)	0.8066 (3)	0.54795 (18)	0.0618 (6)
H221	−0.0386 (10)	0.754 (4)	0.570 (3)	0.075 (10)*
H222	0.0166 (14)	0.717 (4)	0.555 (3)	0.120 (17)*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0302 (6)	0.0478 (8)	0.0185 (6)	−0.0032 (6)	0.0031 (5)	0.0039 (5)
O2	0.0313 (6)	0.0472 (8)	0.0164 (5)	−0.0051 (6)	−0.0040 (4)	0.0036 (5)
N3	0.0316 (7)	0.0335 (8)	0.0181 (6)	−0.0022 (6)	0.0028 (5)	0.0009 (6)
N1	0.0312 (7)	0.0352 (8)	0.0165 (6)	−0.0006 (6)	−0.0012 (5)	0.0012 (6)
C6	0.0330 (8)	0.0390 (10)	0.0245 (8)	−0.0006 (8)	−0.0062 (6)	−0.0016 (7)
C2	0.0291 (8)	0.0258 (8)	0.0148 (6)	0.0024 (6)	0.0012 (5)	0.0000 (6)
C4	0.0354 (9)	0.0361 (10)	0.0289 (9)	−0.0051 (8)	0.0075 (7)	0.0008 (7)
C5	0.0289 (9)	0.0392 (10)	0.0373 (10)	−0.0036 (8)	−0.0006 (7)	−0.0014 (8)
Li1	0.0376 (16)	0.0420 (18)	0.0173 (13)	0.0004 (14)	0.0020 (11)	−0.0006 (12)
O3	0.0754 (12)	0.0358 (8)	0.0277 (7)	0.0017 (8)	−0.0090 (7)	0.0005 (7)
C7	0.0258 (7)	0.0285 (8)	0.0171 (7)	0.0017 (6)	0.0006 (5)	0.0009 (6)
O21	0.0337 (11)	0.0675 (17)	0.0551 (15)	0.000	−0.0086 (10)	0.000
Li2	0.0301 (17)	0.116 (4)	0.0305 (18)	0.009 (2)	0.0030 (14)	0.018 (2)
Cl1	0.0420 (3)	0.0553 (3)	0.0345 (3)	−0.0001 (2)	0.00346 (19)	0.0087 (2)
O22	0.0349 (8)	0.0967 (16)	0.0550 (11)	0.0101 (10)	0.0123 (7)	0.0338 (11)

*Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )*

O1—C7	1.247 (2)	Li1—N3 <sup>iii</sup>	2.221 (4)
Li1—O1	2.069 (3)	Li1—Li2 <sup>iv</sup>	3.414 (6)
O2—C7	1.2528 (19)	O3—H32	0.86 (4)
O2—Li2 <sup>i</sup>	1.968 (4)	O3—H31	0.83 (4)
O2—Li1 <sup>ii</sup>	2.029 (4)	Li2—O21	2.140 (6)
N3—C2	1.333 (2)	O21—Li2 <sup>i</sup>	2.140 (6)
N3—C4	1.335 (2)	O21—H211	0.84 (3)
N3—Li1 <sup>ii</sup>	2.221 (4)	Li2—O22	1.915 (4)
N1—C6	1.337 (2)	Li2—O2 <sup>i</sup>	1.968 (4)
N1—C2	1.338 (2)	Li2—O1	1.993 (4)
Li1—N1	2.175 (4)	Li2—O22 <sup>iv</sup>	2.623 (7)
C6—C5	1.377 (3)	Li2—Li2 <sup>i</sup>	2.856 (8)
C6—H6	0.9300	Li2—Li2 <sup>iv</sup>	3.183 (11)
C2—C7	1.517 (2)	Li2—Li1 <sup>iv</sup>	3.414 (6)
C4—C5	1.379 (3)	Li2—H222	2.343 (18)
C4—H4	0.9300	O22—Li2 <sup>iv</sup>	2.623 (7)
C5—H5	0.9300	O22—H221	0.868 (18)
Li1—O3	1.987 (4)	O22—H222	0.891 (18)
Li1—O2 <sup>iii</sup>	2.029 (4)		
C7—O1—Li2	125.36 (16)	Li2—O21—Li2 <sup>i</sup>	83.7 (3)
C7—O1—Li1	117.79 (15)	Li2—O21—H211	124 (2)
Li2—O1—Li1	116.70 (16)	Li2 <sup>i</sup> —O21—H211	112 (2)
C7—O2—Li2 <sup>i</sup>	124.07 (17)	O22—Li2—O2 <sup>i</sup>	108.02 (19)
C7—O2—Li1 <sup>ii</sup>	117.82 (15)	O22—Li2—O1	98.98 (19)
Li2 <sup>i</sup> —O2—Li1 <sup>ii</sup>	117.32 (18)	O2 <sup>i</sup> —Li2—O1	145.3 (3)
C2—N3—C4	116.42 (15)	O22—Li2—O21	112.7 (3)
C2—N3—Li1 <sup>ii</sup>	108.69 (14)	O2 <sup>i</sup> —Li2—O21	98.6 (2)
C4—N3—Li1 <sup>ii</sup>	134.65 (15)	O1—Li2—O21	90.32 (18)

C6—N1—C2	116.14 (15)	O22—Li2—O22 <sup>iv</sup>	92.4 (2)
C6—N1—Li1	133.22 (14)	O2 <sup>i</sup> —Li2—O22 <sup>iv</sup>	81.1 (2)
C2—N1—Li1	110.62 (14)	O1—Li2—O22 <sup>iv</sup>	76.29 (19)
N1—C6—C5	122.22 (17)	O21—Li2—O22 <sup>iv</sup>	153.3 (2)
N1—C6—H6	118.9	O22—Li2—Li2 <sup>i</sup>	160.4 (2)
C5—C6—H6	118.9	O2 <sup>i</sup> —Li2—Li2 <sup>i</sup>	81.81 (19)
N3—C2—N1	126.11 (16)	O1—Li2—Li2 <sup>i</sup>	79.56 (18)
N3—C2—C7	117.06 (14)	O21—Li2—Li2 <sup>i</sup>	48.13 (14)
N1—C2—C7	116.82 (15)	O22 <sup>iv</sup> —Li2—Li2 <sup>i</sup>	106.04 (10)
N3—C4—C5	122.10 (17)	O22—Li2—Li2 <sup>iv</sup>	55.42 (15)
N3—C4—H4	119.0	O2 <sup>i</sup> —Li2—Li2 <sup>iv</sup>	93.4 (2)
C5—C4—H4	119.0	O1—Li2—Li2 <sup>iv</sup>	84.2 (2)
C6—C5—C4	116.98 (18)	O21—Li2—Li2 <sup>iv</sup>	165.6 (3)
C6—C5—H5	121.5	O22 <sup>iv</sup> —Li2—Li2 <sup>iv</sup>	36.95 (15)
C4—C5—H5	121.5	Li2 <sup>i</sup> —Li2—Li2 <sup>iv</sup>	142.6 (2)
O3—Li1—O2 <sup>iii</sup>	103.68 (16)	O22—Li2—Li1 <sup>iv</sup>	82.13 (16)
O3—Li1—O1	91.92 (15)	O2 <sup>i</sup> —Li2—Li1 <sup>iv</sup>	31.87 (10)
O2 <sup>iii</sup> —Li1—O1	107.96 (16)	O1—Li2—Li1 <sup>iv</sup>	139.6 (3)
O3—Li1—N1	127.32 (18)	O21—Li2—Li1 <sup>iv</sup>	126.81 (17)
O2 <sup>iii</sup> —Li1—N1	128.74 (19)	O22 <sup>iv</sup> —Li2—Li1 <sup>iv</sup>	63.32 (13)
O1—Li1—N1	78.11 (12)	Li2 <sup>i</sup> —Li2—Li1 <sup>iv</sup>	111.75 (17)
O3—Li1—N3 <sup>iii</sup>	92.14 (15)	Li2 <sup>iv</sup> —Li2—Li1 <sup>iv</sup>	63.10 (15)
O2 <sup>iii</sup> —Li1—N3 <sup>iii</sup>	78.36 (12)	O22—Li2—H222	21.2 (6)
O1—Li1—N3 <sup>iii</sup>	171.42 (18)	O2 <sup>i</sup> —Li2—H222	124.0 (7)
N1—Li1—N3 <sup>iii</sup>	93.42 (14)	O1—Li2—H222	88.1 (8)
O3—Li1—Li2 <sup>iv</sup>	102.75 (17)	O21—Li2—H222	94.7 (9)
O2 <sup>iii</sup> —Li1—Li2 <sup>iv</sup>	30.81 (10)	O22 <sup>iv</sup> —Li2—H222	107.6 (10)
O1—Li1—Li2 <sup>iv</sup>	77.24 (13)	Li2 <sup>i</sup> —Li2—H222	140.1 (7)
N1—Li1—Li2 <sup>iv</sup>	124.23 (17)	Li2 <sup>iv</sup> —Li2—H222	71.8 (9)
N3 <sup>iii</sup> —Li1—Li2 <sup>iv</sup>	109.16 (14)	Li1 <sup>iv</sup> —Li2—H222	102.2 (6)
Li1—O3—H32	129 (3)	Li2—O22—Li2 <sup>iv</sup>	87.6 (2)
Li1—O3—H31	126 (2)	Li2—O22—H221	119 (2)
H32—O3—H31	101 (3)	Li2 <sup>iv</sup> —O22—H221	117 (2)
O1—C7—O2	127.12 (16)	Li2—O22—H222	107.6 (17)
O1—C7—C2	116.22 (14)	Li2 <sup>iv</sup> —O22—H222	135 (3)
O2—C7—C2	116.65 (15)	H221—O22—H222	93 (2)

Symmetry codes: (i)  $-x, y, -z+1/2$ ; (ii)  $x, -y+2, z-1/2$ ; (iii)  $x, -y+2, z+1/2$ ; (iv)  $-x, -y+2, -z+1$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O22—H222 $\cdots$ O3	0.89 (2)	2.16 (3)	2.841 (3)	133 (3)
O22—H221 $\cdots$ Cl1 <sup>v</sup>	0.87 (2)	2.36 (2)	3.212 (2)	167 (3)
O3—H31 $\cdots$ Cl1	0.83 (4)	2.35 (4)	3.1381 (19)	158 (3)
O3—H32 $\cdots$ Cl1 <sup>vi</sup>	0.86 (4)	2.29 (4)	3.1429 (19)	168 (4)
O21—H211 $\cdots$ Cl1 <sup>vii</sup>	0.84 (3)	2.45 (3)	3.288 (2)	175 (3)

Symmetry codes: (v)  $-x, y, -z+3/2$ ; (vi)  $x, -y+1, z-1/2$ ; (vii)  $-x, -y+1, -z+1$ .